

## **Marine Chemistry Special Issue: The Renaissance of Radium Isotopic Tracers in Marine Processes Studies**

### **Guest Editors**

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Four radium isotopes, decay products of the  $^{238}\text{U}$ - $^{232}\text{Th}$ - $^{235}\text{U}$  series radionuclides, occur in nature:  $^{224}\text{Ra}$  ( $t_{1/2}=3.66$  days),  $^{223}\text{Ra}$  ( $t_{1/2}=11.4$  days),  $^{228}\text{Ra}$  ( $t_{1/2}=5.75$  years), and  $^{226}\text{Ra}$  ( $t_{1/2}=1600$  years). Beginning with the GEOSECS program of the late 1960s-early 1970s, these radium isotopes have been widely applied to the study of a variety of oceanographic processes (Moore, 1972; Trier et al., 1972). In the GEOSECS era, upper-ocean and bottom boundary layer mixing were quantified using  $^{228}\text{Ra}$  (Sarmiento et al., 1976). Coastal ocean mixing was a notable application of the radium quartet in the 1980s (Moore, 1987).

Beginning in the mid-1990s, radium underwent a renaissance in the ocean sciences, when it was used to quantify the importance of submarine groundwater discharge (SGD) on the oceanic budget of many trace metals and nutrients (Moore, 1996; Burnett et al., 2006 and references therein; Fig. 1). Concurrent with this discovery was the production of a commercially available delayed coincidence counter (RaDeCC; Moore and Arnold, 1996), which greatly simplified the measurement of the two short-lived Ra isotopes,  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$ .

This heightened level of interest in Ra isotopes precipitated the organization of a workshop on “measurements of short-lived radium isotopes using the RaDeCC delayed coincidence system”. The scope of the workshop not limited to RaDeCC applications; other key subject areas included interpretation and modeling of radium measurements in marine systems as well as perspectives on special challenges and future applications.

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The workshop was held in Monaco during October 2-6, 2006 and was hosted by the Marine Environment Laboratories, International Atomic Energy Agency (IAEA-MEL). There were 26 participants from laboratories around the world; by the end of the meeting, there was strong support for the creation of a special issue of *Marine Chemistry*. Many of the 14 oral presentations are represented as publications in this volume.

The powerful radioactive “clocks” associated with the short-lived radium isotopes have seen greatly increased application since the advent of RaDeCC. Moore (2008) provides a valuable update on the operation and application of this counting system. Dimova et al. (2008) investigate the appropriate procedures to produce standard Mn-fibers required to calibrate the RaDeCC measurements. Garcia-Solsona et al. (2008) perform a detailed error propagation analysis of the uncertainties associated with RaDeCC determination of  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$ .

Two papers deal with analytical improvements or advances in the measurement of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in marine systems. Ollivier et al. (2008) use thermal ionization mass spectrometry in an attempt to quantify SGD in a coastal French embayment. Due to the extremely low levels in open ocean systems, a number of methods for preconcentration of Ra isotopes from seawater have been developed; Borquin et al. (2008) set out to evaluate these techniques in the Southern Ocean surrounding the Kerguelen Plateau. Most of the data on 227-actinium in the ocean were obtained using the RaDeCC system and in the paper of Geibert et al. (2008), a global compilation of available data highlight the potential of  $^{227}\text{Ac}$  as a tracer for diapycnal mixing. In a companion contribution, Geibert & Vöge (2008) explore alternative analytical methods that greatly facilitate  $^{227}\text{Ac}$  measurements in seawater.

A number of contributions to this volume add to the growing literature on SGD. Beck et al. (2008) conclude that SGD consisted of 90% recirculated seawater within a coastal embayment on Long Island, NY (USA). In the arid Adelaide region of South Australia, Lamontagne et al. (2008) observe an even greater proportion of seawater in the SGD. Using Si in addition to Ra isotopes as a tracer, Street et al. (2008) determine that SGD supplies significant quantities of nutrients to the coastal zone and coral reef ecosystems of several Hawaiian Islands (USA). In another tropical setting (Celestun Lagoon, Mexico) Young et al. (2008) identify two different

types of submarine groundwater sources with seasonally variable fluxes. Kim et al. (2008) contrast winter and summer SGD and associated nutrient flux in Yeongil Bay (Korea). The chemical processes controlling the release of radium from the sediments to groundwater aquifers as well as the reverse adsorption reactions are the subjects of an investigation by Gonneea et al. (2008). The seasonality of the radium cycling observed in this study corroborates findings by Hougham et al. (2008), who observe seasonally variable porewater radium concentrations in Rhode Island coastal pond sediments. The tagging of coastal waters by  $^{224}\text{Ra}$  and  $^{223}\text{Ra}$  are exploited by Dulaiova and Burnett (2008) to constrain the flushing rates of Apalachicola Bay, Florida (USA). Garcia-Solsona et al. (2008) estimate that the SGD flux to the northern Venice Lagoon flux is of the same order of magnitude as the riverine flux, but most of this SGD consists of recirculated seawater. In a deep-water application, Moore et al. (2008) use short-lived Ra isotopes to infer large fluid fluxes through the Puna Ridge off the Hawaiian Islands.

### **Future Directions**

Radium isotopes and radon will continue to play an integral role in future submarine groundwater studies. Further applications of these isotopes (including  $^{227}\text{Ac}$ ) are expected to help constrain the sources and sinks of key trace elements and their isotopes (TEIs) in the upcoming GEOTRACES program: “the international study of the marine biogeochemical cycles of TEIs”. In addition to constraining the land-ocean transport of TEIs, radium, radon, and actinium may be used to quantify a wide range of GEOTRACES processes from the release of Fe and Mn in oxygen minimum zone sediments to vertical water mass mixing to lateral sediment transport in nepheloid layers.

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## Figure Captions

Figure 1. Number of publications per year (1998-2007) having the keywords (a) “radium AND ocean” and (b) “radium AND groundwater”. Many publications from 1996 onward may fall into both categories. In addition, the second search includes a number of terrestrial groundwater Ra studies; however, the sharp increase beginning in 1999 is largely due to the addition of SGD studies. Data source: Science Citation Index, Web of Science.